

# **Water Quality Concerns Related to Personal Watercraft Usage**

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May 27, 1999

## ***Introduction***

Nearly all personal watercraft (PWC) utilize conventional two-stroke engines. As much as 30 percent of the fuel used by these engines is discharged unburned into water [1]. The combustion process discharges additional toxic compounds into water. As a result, the use of PWCs has resulted in measurable water quality degradation in the nation's lakes and reservoirs.

The following components of the fuel are discharged to the receiving water: benzene, toluene, ethyl benzene, xylene (collectively called BTEX), and methyl tertiary butyl ether (MTBE). Polycyclic aromatic hydrocarbons (PAHs) are discharged to water in small amounts as part of the unburned fuel and in much larger amounts as part of the exhaust from engine combustion. Because of its chemical characteristics, BTEX readily transfer from the water to air whereas MTBE and PAHs do not. MTBE and PAHs have been found in lakes and reservoirs with PWC usage, sometimes at levels in excess of human health and ecologic risk standards.

This report has been written to:

- document concentrations of MTBE and PAHs found in lakes and reservoirs in the U.S. as a result of recreational watercraft usage;
- identify the risks that MTBE and PAHs pose to humans and aquatic organisms;
- describe management strategies that have been taken by other agencies to address concerns posed by these contaminants;
- interpret the results of these studies to determine the water quality concerns related to PWC usage; and
- provide a list of helpful references on this topic.

## ***Combustion Process***

### **Conventional Two-Stroke Engines**

Also known as "two-cycle" engines, these motors intake a mixture of air, gasoline, and oil into the combustion chamber while exhaust gases are being expelled from the combustion chamber. Since the intake and exhaust processes are occurring at the same time, it is unavoidable that some of the unburned fuel mixture will escape with the exhaust. This expulsion of unburned fuel is the reason for the elevated levels of hydrocarbon emissions from conventional two stroke engines. Hydrocarbon emission levels for conventional two-stroke outboard or PWC motors range from approximately 100 grams/kw-hr to more than 300 grams/kw-hr [2]. Based on average use, a typical conventional two-stroke outboard or PWC will expel as much as 30% of the incoming

fuel mixture, unburned, via the exhaust. At common fuel consumption rates, an average two-hour ride on a PWC may discharge three gallons of the gas-oil mixture into the water.

### **Direct-Injection Two-Stroke Engines**

These new engines also have concurrent intake and exhaust processes; however, unlike the conventional two-strokes, the intake charge is air only (no fuel is mixed into the intake charge). The fuel is injected directly into the combustion chamber only after the exhaust process has finished. This means that no unburned fuel escapes with the exhaust. This results in a four-fold decrease in smog-forming pollution in a typical 90-horsepower engine when compared to a conventional two-stroke [1]. However, these emissions from direct-injected two-strokes are still four times higher than four-stroke engines with the same horsepower [1].

### **Regulatory Requirements**

In December 1998, the California Air Resources Board adopted new emission regulations for gasoline-powered marine engines, including outboard, PWC, and some jet boat engines [1]. The regulations apply only to new marine engines manufactured for the 2001 model year and later. There is no requirement to retrofit pre-2001 model year watercraft or engines.

Under California Air Resources Board's new regulations, a typical marine engine will become 75% cleaner by 2001 and 90% cleaner by 2008. The reduction in pollution will be achieved, in part, through the use of direct-injection two-stroke engines with catalytic converters.

### **Direct-Injection Engine Availability**

PWC manufacturers are currently in the process of introducing direct-injection engines. The first direct-injection PWCs debuted late in the 1998 model year. It is expected that most manufacturers in the U.S. market will offer a full range of direct-injection outboard and PWC engines by approximately 2002, partly in response to the demands imposed by California and Federal regulators.

### ***Contaminants***

#### **MTBE**

##### Background

The addition of oxygenates, such as MTBE and ethanol, to gasoline has become more common in recent years. These oxygenates enhance octane level, increase burning efficiency, and reduce the emission of atmospheric pollutants. The most frequently used oxygenate is MTBE which is used in 17 states to meet air quality standards [3]. According to EPA's Office of Mobile Sources, about 30% of U.S. gasoline currently contains some form of oxygenate for air quality improvement purposes at levels up to 15% by volume. More than 10 billion kg of MTBE were used in U.S. gasoline in 1996 [4], making MTBE the second-most widely produced chemical in the U.S. [5].

MTBE is difficult to remove from contaminated water because of its high water solubility and low volatility. Most water treatment plants would have little or no effect in reducing MTBE concentrations from the raw water supply without expensive system upgrades.

MTBE can contaminate surface water through point-source releases such as underground storage tank leaks. MTBE can also contaminate surface water through non-point releases such as stormwater runoff. The contamination of lakes and reservoirs with MTBE has been documented where PWCs are used. The recreational use of two-stroke motors has been identified as a primary cause of this contamination. In general, lakes and reservoirs with greater degrees of recreation show higher concentrations of MTBE, particularly in the summertime and in upper water layers [6].

The State of California has adopted a secondary drinking water standard of 5 µg/L (microgram per liter or part per billion) for MTBE on the basis of taste and odor [7]. California has also proposed a primary, health-based drinking water standard of 13 µg/L for MTBE [7].

#### MTBE in Surface Water

The Metropolitan Water District (MWD) of Southern California has conducted an extensive MTBE monitoring program in six surface water reservoirs of varying recreational activity [6]. The occurrence of MTBE correlated with the general pattern of recreational use by motorized watercraft. These investigators determined seasonal trends at Lake Perris and found that concentrations of MTBE reached as high as 25 µg/L at the lake surface in the summertime, a level exceeding California's primary drinking water standard of 13 µg/L. MTBE was found in concentrations up to 8 µg/L in Lake Perris in the fall and winter as the lake mixed vertically, a level exceeding the 5 µg/L California secondary maximum contaminant level (MCL) [6].

Concentrations of MTBE in and around marinas, or in other areas expressly used for boating, can be much higher [8]. In Shasta Lake, a large hydropower and recreational-use reservoir in northern California, concentrations ranged from 9-88 µg/L over the Labor Day 1996 weekend. Maximum values were associated directly with large boats entering a docking area or with engine exhaust from these same vessels. MTBE was also measured in a temporary lake constructed in southern California for a jetski event in the summer of 1996. After the three-day event, concentrations ranged from 50-60 µg/L and were well mixed in this shallow water body. Concentrations of MTBE at Lake Tahoe in the vicinity of boating activity were often within the range of 20-25 µg/L, with a single maximum measured value of 47 µg/L [8].

Since March 1997, one of the most extensive efforts to monitor MTBE to date has been conducted at Donner Lake, California [8]. The ongoing research at Donner Lake has indicated the following:

- Of the 470 samples analyzed to date, MTBE concentrations have ranged from 0.09 to 12.1 µg/L;
- Concentrations of MTBE appear to be uniformly distributed throughout the entire surface area of the lake;
- Residual concentrations carried over from 1996 to 1997 are in the range of 0.1-0.2 µg/L;
- Beginning in early May, and coincident with the onset of the summer boating season, MTBE concentrations in the surface waters increased from a low value of 0.1 µg/L on April 24th to approximately 2 µg/L just prior to the 4th of July weekend;
- Sampling on July 7 showed a dramatic six-fold increase of MTBE in surface water from 2 to 12 µg/L. This increase is most likely the result of increased fuel exhaust into Donner Lake

from 2-stroke engine watercraft since rainfall and urban runoff was negligible at this time, and since stream flow was nearing its seasonal minimum;

- MTBE in the upper and warmer portion of the lake (0-35 feet deep) was uniformly high as the result of natural wind mixing of these waters. Below approximately 50 feet in the colder uncirculated waters, MTBE was always less than 0.5 µg/L. This distinct distribution results from the formation of a stable density boundary in the lake which prevents mixing between the surface and bottom waters; and
- During March and April, before boating activity increased on the lake, it was calculated that Donner Lake contained 45-65 pounds of MTBE. By July 1, this had increased to 250 pounds with a sharp increase to a maximum of 815 pounds shortly after the July 4th holiday. Over the September Labor Day weekend, MTBE also increased but much less dramatically (i.e., approximately a 100-pound increase).

## PAHs

### Background

PAH molecules contain two to seven benzene rings. Their environmental fate, persistence, and toxicity are related to this molecular structure and to the number and configuration of attached alkyl groups (such as methyl (CH<sub>3</sub>-) or ethyl (CH<sub>3</sub>CH<sub>2</sub>-) groups). The smaller and lighter (i.e., two- and three-ringed) compounds are generally more water-soluble, more biodegradable, and more volatile. Their solubility makes them more bioavailable (and more of a risk) to aquatic life, but their low persistence also reduces exposure times. The larger and heavier (i.e., four- through seven-ringed) compounds are generally much less water soluble, bind more strongly to sediment and tissue of exposed organisms, and don't biodegrade or volatilize as easily. PAHs (light or heavy) with alkyl groups attached are more persistent and more likely to bind to sediment and tissue than the non-alkylated "parent" PAH compounds. The lighter PAHs are generally thought to be more of an immediate (acute) threat to organisms in the water column, while the heavier PAHs (including the alkyl PAHs) tend to be a longer-term (chronic) threat to sediment-dwelling organisms. Recent studies (as discussed herein), however, are showing a wider range of PAHs (including the heavy and alkyl PAHs) to also be in the water and be a risk to aquatic life. Some consider the possible effects of a PAH-contaminated sediment accumulating in the benthic zones of lakes/reservoirs to be a more serious, but currently less understood, risk to aquatic life. (This paper, however, does not specifically address sediment; for more on PAHs, alkyl PAHs, and PAHs in sediment, see the NPS "Contaminants Encyclopedia" at <http://www.aqd.nps.gov/toxic>

### PAHs in Surface Water

PAHs in unburned ("petrogenic") two-stroke fuel mixture are rare, with the possible exception of naphthalene and acenaphthene. The combustion process of the two-stroke engine, however, creates several different combustion ("pyrolytic") PAHs (including alkyl PAHs) that have been found in the water.

At least three different studies have linked motorboat usage to PAH contamination of water. One study found PAHs in the Occoquan Reservoir, a drinking-water source east of Washington, D.C. [9]. Total PAH concentrations in the water column (5-25 ft. deep) were as high as 4.12 µg/L. The most common PAHs were phenanthrene, pyrene, chrysene/benzo(a)anthracene, benzo(a)pyrene, and acenaphthene. A sample from the surface of the water at a marina was also taken which found 11 different PAHs, including those listed above plus naphthalene, acenaphthylene, anthracene,

fluorene, and flouranthene. This sample had a total PAH concentration of 18.86 µg/L; naphthalene, acenaphthylene, and acenaphthene were each at about 1 µg/L, and phenanthrene, pyrene, chrysene/benzo(a)anthracene, and benzo(a)pyrene were each at 2.3 µg/L or more. The PAH compounds found in the reservoir were mostly indicative of burned fuel, although some PAHs associated with unburned fuel were also present.

These PAHs were found during the month of June when boating activity was highest, and no PAHs were found at the same sample sites in October when boating activity was low, thus indicating their association with motorboats [9]. This is in agreement with another study at Lake Metigoshe, North Dakota, which found the highest hydrocarbon concentrations in July, a time of peak boating activity, and the lowest concentrations in October, a time of low boating activity [9]. Additionally, a 1997 study of motorboat pollutants in Lake Tahoe, CA/NV, found good correlation between peak boating activity and lake PAH concentrations [10].

## ***Human Health Risks***

### **MTBE**

California has adopted a Public Health Goal (PHG) of 13 µg/L for MTBE in drinking water [7]. The PHG is a concentration of a contaminant in drinking water that does not pose any significant risk to health. The PHG for MTBE is based on carcinogenic effects observed in experimental animals. California Department of Health Service will consider the PHG in establishing a primary drinking water standard (maximum contaminant level, or MCL) by July 1, 1999 and will probably set the MCL at the level of the PHG, if technical feasibility and costs allow. The U.S. EPA adopted an advisory level of 20-40 µg/L for drinking water in 1997 [7].

California's secondary MCL for MTBE is 5 µg/L and was made effective January 7, 1999 [7]. Secondary MCLs address "aesthetic" qualities of drinking water supplies. In the case of MTBE, the purpose of the secondary MCL is to protect the public from exposure to MTBE in drinking water at levels that can be smelled or tasted.

### **PAHs**

Of the PAHs found in the Occoquan Reservoir [9], benzo(a)anthracene, benzo(a)pyrene, and chrysene are probable human carcinogens [11]. On this basis, U.S. EPA has established an MCL for benzo(a)pyrene of 0.2 µg/L. MCLs for other PAHs have not been established.

For some of the PAHs associated with two-stroke engines (e.g., those observed in the Occoquan Reservoir study [9]), U.S. EPA has established the following water quality criteria for the protection of human health from exposure to PAHs in drinking water and in the tissue of edible aquatic organisms (e.g., fish) [12]:

Contaminant	Consumption of water and organisms (e.g., fish) (µg/L)	Consumption of organisms (e.g., fish) only (µg/L)
Anthracene	9,600	110,000
Flourene	1,300	14,000
Acenaphthene	1,200	2,700
Benzo(a)anthracene	0.0044*	0.049*

Flouranthene	300	370
Pyrene	960	11,000
Chrysene	0.0044*	0.049*
Benzo(a)pyrene	0.0044*	0.049*

\* based on a one-in-a-million chance of getting cancer

Assuming the Occoquan Reservoir PAH concentrations are indicative of concentrations in other water bodies, some of the above criteria are probably being regularly exceeded in many other water bodies at least several months out of the year.

## ***Ecologic Risks***

### **MTBE**

There is little known about the ecologic risk to aquatic organisms from MTBE. One of the most thorough studies to date [13] found:

- There is little toxicity of MTBE to aquatic organisms, with the most sensitive taxonomic group tested being green algae;
- Fish accumulate MTBE to about 1.5 times the concentration of MTBE in the water column;
- The most conservative hazard quotients for rainbow trout exposed to MTBE in two selected surface waters range from  $1 \times 10^{-3}$  to  $6 \times 10^{-3}$ , well below the level that indicates potential adverse ecological effects; and
- Adverse effects on rainbow trout are not expected until concentrations of MTBE in the water column reach 4,600 µg/L to 4,700 µg/L. These levels are much greater than the human health standards for MTBE in drinking water supplies.

This study, which was a screening-level risk assessment, identified several areas for further research, including: the potential ecological risk to benthic invertebrate communities from MTBE; the combined toxicity from MTBE and other common constituents of gasoline to aquatic organisms; long-term investigations of MTBE toxicity; and other fish tissue studies that include species in addition to trout.

### **PAHs**

Since there are no U.S. EPA National Recommended Water Quality Criteria (neither acute nor chronic) for PAHs [12], one must turn to the literature for concentrations that pose a risk to aquatic life.

One of the more prominent studies [10] found that ambient levels of PAHs in two-stroke motorboat emissions had significant negative impacts on fish growth and zooplankton survival and reproduction in Lake Tahoe. Lake PAH levels ranged from 0.005-0.070 µg/L. The study found that the toxicity of about half of the 15 or so PAHs measured in the water increased in the presence of sunlight. No-observed-effect-concentrations (NOEC) for these PAH phototoxins were calculated as follows: 0.009 µg/L for fish (fathead minnow) growth; 0.007 µg/L for zooplankton (*Ceriodaphnia dubia*) survival; and 0.003 µg/L for zooplankton reproduction. Although samples for the study were collected at a depth of three meters (m), the study predicts that PAH toxicity at these levels could be found as deep as 20 m in Lake Tahoe. This is not

necessarily true for most lakes/reservoirs, however, since Lake Tahoe is highly oligotrophic and has a high degree of clarity (low turbidity).

NOTE on phototoxicity: Much of the PAH toxicity data from the literature that resource managers compare field data to (e.g., PAH concentrations measured in a water body) do not take into account phototoxicity. The toxicity of certain PAHs in the presence of sunlight or UV light can be hundreds of times greater than would be the case in the absence of photo sources [14,15,16]. Giesy states that the toxicity of some PAHs found in two-stroke exhaust is as much as 50,000 times more toxic in field (sunlit) conditions than in laboratory (unexposed to UV light) conditions [17]. The phototoxic effect is very important to consider when determining safe/acceptable levels of PAHs in water. The results from the Lake Tahoe study [10], therefore, are especially informative because they were attained using field conditions—like sunlight (UV) and water samples from the Lake—for their toxicity tests. Other studies also have documented the phototoxicity (to the zooplankton *Daphnia magna*) of several PAHs [18].

Two studies by Tjarnlund, et al., exposed fish to two-stroke motor exhaust levels that would be found in or near the wake of such a boat. All exhaust components—not just PAHs—were included in these studies. One study found several different morphological disturbances in fathead minnows, and elevated levels of DNA-adducts in the blood, liver, and kidneys of perch [19]. The other study found disruption of biological functions in rainbow trout at different levels of biological organization including cellular and subcellular processes (DNA-adduct levels and enzyme activity) and physiological functions (carbohydrate metabolism) [20].

Two other recent studies measured the toxicity of PAHs from crude oil to fish. Some of the PAHs involved in these studies also have been found in the burned-fuel component of two-stroke discharge. In the first, total PAH concentrations (from weathered crude oil) of 0.7 µg/L caused malformations, genetic damage, mortality, decreased size, and inhibited swimming in Pacific herring eggs; concentrations of 0.4 µg/L caused sublethal responses such as yolk sac edema and immaturity consistent with premature hatching [21]. In the second, experiments with Pink salmon embryos led the authors to conclude that water quality standards for total PAHs above 1.0 µg/L may fail to protect fish embryos; they suggest a standard of only 0.010 µg/L (includes a safety factor of ~100x) [22].

NOTE: It is important to note that this suggested standard be based on both “parent” PAH *and* alkyl PAH measurements. Most total PAH analyses do not use laboratory methodologies that detect the alkyl PAHs, thus underestimating—often grossly so—true total PAH concentrations and the risk they pose. To use standards or criteria that are based on both “parent” and alkyl PAHs properly would require analyzing water samples (or sediment, soil, or tissue) for the same PAHs. This discrepancy between the PAHs that are actually out in the environment and those that usually are actually measured or used to calculate standards and criteria is a growing controversy among environmental toxicologists. This explains why many in the field require that the so-called “expanded” PAH scan be conducted when measuring PAH concentrations in environmental samples. (See reference [23] for a description of this analytical method.)

## ***Actions by Water Management Agencies***

On the basis of concerns for contamination of water supplies used for human consumption, at least five water management districts have banned or restricted the use of motor boats, including PWCs, on reservoirs in California [24]. These agencies include Metropolitan Water District (MWD) of Southern California, East Bay Municipal Utility District (East Bay MUD), Contra Costa Water District, Santa Clara Valley Water District, and Tahoe Regional Planning Agency. East Bay MUD has proposed to ban all two-stroke engines, including direct-injection, by January 1, 2000.

Some of the current restrictions include selective bans on PWCs in the summer and fall months. The banning of PWC usage as opposed to other types of watercraft is based on studies that show PWCs impart a disproportionate amount of pollution to water. Data from one study of PWCs and outboard motorboats show that PWCs emitted 80% of the hydrocarbons while representing one third of the watercraft [25]. PWCs use more fuel and discharge more pollution to water than other watercraft with outboard two-stroke engines because they are designed and operated differently. PWCs have a narrow hull that rides low or sinks in the water. To get the hull to plane more efficiently on the surface of the water, operators commonly open the throttle fully to "give it gas." Additionally, PWCs tend to sink when performing common stunts at lower speeds and the throttle must be fully opened to complete the maneuvers.

Water management agencies are also selectively drawing water from depths below those where the highest MTBE concentrations are found. This is only an option at lakes where depth-specific intake structures have been constructed and where MTBE is concentrated in the upper part of the water column [6]. MWD has documented MTBE to be uniformly distributed throughout the water column at 4 µg/L in Lake Perris in Southern California. If motorboat usage were to increase at that lake, it is possible that the secondary MCL of 5 µg/L could be exceeded, no matter what the intake depth. Typical water treatment plants have little or no effect in reducing MTBE concentrations from the raw water supply.

## ***Conclusions***

- The use of two-stroke engines, including PWCs, has resulted in the contamination of lakes and reservoirs. MTBE and PAHs are commonly observed two-stroke contaminants and pose the most serious threats to human and ecological health. Concentrations of MTBE in lakes in California routinely exceed State human health standards and taste and odor thresholds. At drinking water intakes in these lakes, concentrations of MTBE have, on occasion, exceeded the taste and odor threshold. Water treatment facilities are generally ineffective in reducing MTBE concentrations. Therefore, with increasing motorboat use, unacceptable tastes and odors as well as health risks could be posed to drinking-water consumers. Aquatic ecologic communities do not appear to be threatened by observed concentrations of MTBE; however, more research is needed to reinforce this conclusion.
- PAH concentrations in lakes and reservoirs with high motorboat activity have been found at levels dangerous to aquatic organisms. The concentrations causing adverse effects can be extremely low (parts-per-trillion range) due to PAH phototoxicity, especially in oligotrophic waters where sunlight penetration is high. Some are concerned about possible adverse effects from PAHs bound to sediment, especially in waters higher in suspended solids; this



phenomenon is currently poorly understood. PAH concentrations in lakes and reservoirs with high motorboat activity also have been found at levels dangerous to human health where humans are drinking the water and/or consuming the fish from these waters. Although PAH concentrations have not been widely measured, there is no reason to believe that the concentrations quoted from the studies above are not widespread in lakes or reservoirs with high motorboat activity.

- Management strategies adopted by other agencies include outright bans on PWC and restricted use of two-stroke motors. The exclusive use of the newly introduced and less polluting, direct-injection two-stroke engines has also been examined by water management agencies. Other strategies include drawing relatively uncontaminated water from deeper intervals to supply drinking water.

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